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# Assessing Photocatalytic Activity Using Methylene Blue without Dye Sensitisation

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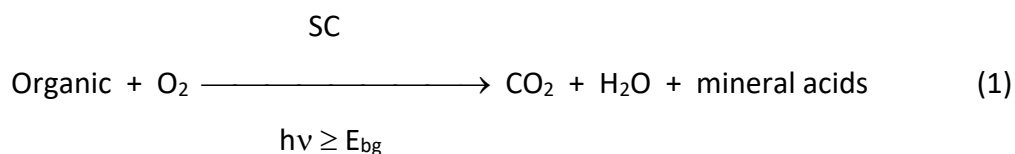
## Abstract

The anaerobic photocatalysed reduction of methylene blue, MB, by glycerol to leuco methylene blue, LMB, is studied using UV-absorbing, P25 TiO<sub>2</sub>, and visible-absorbing, CdS, semiconductor powder particles as the photosensitizer. In both cases, the photo-reductive bleaching of the dye to LMB, is very rapid, typically < 2 min. The photobleaching of the MB is readily and simply reversed in the dark by allowing air into the system, so as to let the ambient oxygen to oxidise the photogenerated LMB back to its original blue, oxidized form, MB. Action spectra are recorded for both systems and reveal no evidence of dye-sensitisation, nor dye photolysis over the time scale of the reaction (i.e. ca. 2 min). Instead, the action spectra exhibit spectral profiles that match very well that of the diffuse reflectance spectra of the respective semiconductor photocatalysts. The MB/glycerol system appears to offer a simple, quick, unambiguous way to assess the photocatalytic activity of both visible and UV absorbing photocatalyst powders using a dye, such as MB.

**Key words:** action spectrum, methylene blue, reductive photocatalysis, titanium dioxide, cadmium sulfide

## Introduction

Most photocatalytic, commercial materials use a semiconductor, SC, which is  $\text{TiO}_2$ , to mediate the photo-oxidation of organic species, in solid, dissolved or gaseous form, to minerals, with the concomitant reduction of ambient  $\text{O}_2$  to water [1,2], i.e.



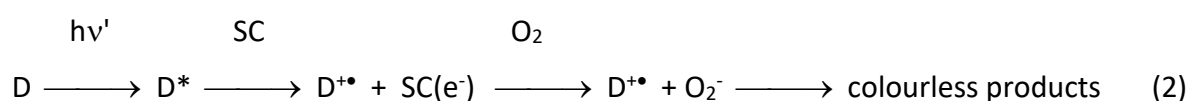
where,  $h\nu$  is the energy of the incident light which is greater than, or equal to, the bandgap energy of the SC,  $E_{\text{bg}}$ , and where too, mineral acids are generated if the organic species possesses one or more heteroatoms, such as S, Cl or N, in its structure [1,2]. In research, and industry, it is essential to be able to assess and compare the activities of new and existing photocatalytic materials. Thus, it is not surprising to note that in recent years a number of different tests for this purpose have been developed into ISO standards [3]. These tests include: the photo-oxidative bleaching of a dye, methylene blue, MB, in aqueous solution [4], i.e. reaction (1), with organic = MB, where the semiconductor photocatalyst is in film form.

ISO tests are essential for comparing the activities of different commercial products, even though such tests are often quite involved and time-consuming [4]. Interestingly, most of these tests are for photocatalytic films and there is not, as yet, an ISO standard for testing photocatalysts in powder form, which is unfortunate since, in research, many new photocatalysts are produced initially in powder form.

For many years, the most popular approach to assess the photocatalytic activities of powdered SCs was to disperse the semiconductor photocatalyst powder under test in an aqueous solution of a dye, such as MB or Acid Orange 7, AO7, and monitor the rate of photobleaching of the dye, which is presumed to be *via* the oxidation reaction (1) [5]. This photocatalysed dye-oxidation method is very attractive in that it is usually fast, easy to employ and monitor and striking in effect; indeed this latter feature makes it ideal for demonstrating the efficacy of photocatalysis to a wider audience. Unfortunately, it is flawed in that it is really only appropriate when the excitation light, i.e.  $h\nu$ , cannot be absorbed by the dye itself, otherwise dye sensitization or photolysis, rather than

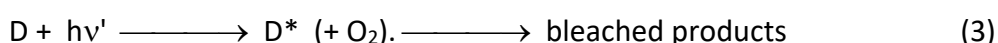
photocatalysis, may be responsible for the observed change (usually loss) in the original colour of the dye [5-7].

The process of dye (photo)sensitisation typically involves the initial electronic excitation of the dye, D, to D\*, by light of appropriate energy,  $h\nu'$ , so that D\* is then able to inject an electron into the conduction band of the semiconductor, SC [5-8]. The injected electron is then able to react with ambient O<sub>2</sub>, while the unstable, oxidized dye radical, D<sup>•+</sup>, decomposes to form colourless products [5,7-9]. The process can be summarized as follows:



A classic example of dye sensitization is provided by the study Zhang *et al.* of the photosensitized bleaching of Eosin under visible light in an aerated, aqueous dispersion of P25 TiO<sub>2</sub> [10]. This work showed that light absorbed by the dye alone was able to effect its rapid and complete photobleaching. Another very important example of dye-sensitisation is the study of Ohtani and his co-workers [11], of the photobleaching of MB by P25 TiO<sub>2</sub> using visible light. These researchers measured the photonic efficiency,  $\eta$ , for the visible photobleaching of the MB, as a function of incident radiation wavelength,  $\lambda$  and found that the resulting action spectrum, i.e.  $\eta$  vs.  $\lambda$  plot, was similar in shape to that of the diffuse reflectance spectrum, DRS, of the MB adsorbed onto the TiO<sub>2</sub>, with a peak at ca. 665 nm light, which is the wavelength of maximum absorption in the visible,  $\lambda_{\text{max}}$ , for MB [11].

In contrast, dye photolysis involves the electronically excited state of the dye which is either simply unstable and/or quenched by ambient O<sub>2</sub> to produce singlet oxygen [10] – which then oxidises the dye, i.e.



Given reaction (3), it is not surprising to note that the rate of dye bleaching due to photolysis is often unchanged in the absence and presence of the semiconductor.

The possibility of dye sensitization, and/or dye photolysis, means that the use of MB in reaction (1,) should really be restricted to probing the activities of UVA-absorbing photocatalysts only, since MB absorbs little in that region and, indeed, the MB ISO [4,12],

for photocatalytic films specifies that it is for UVA (NOT visible) excitation only. As a consequence, there is currently no accepted, **unambiguous**, simple photocatalysed dye-destruction method for testing the **visible light** activity of a photocatalytic film or powder and this paper proposes a new approach to resolve this issue.

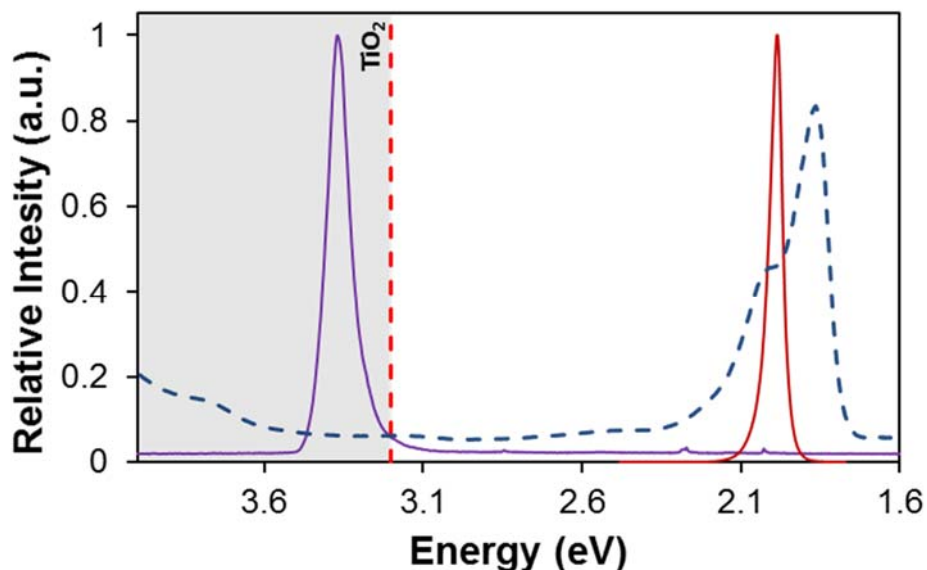
## **Experimental**

### **Materials**

P25 titania (specific surface area (SA) = 53 m<sup>2</sup> g<sup>-1</sup>) was supplied by Degussa (Evonik) and, unless otherwise stated, all other materials were purchased from Sigma Aldrich and used as received, including the sacrificial (i.e. irreversible) electron donor, SED, glycerol. The CdS (SA = 54 m<sup>2</sup> g<sup>-1</sup>) was supplied by Sigma Aldrich and was 99.995% pure. UV-vis spectra were recorded using an Agilent Technologies Cary 50 UV-vis spectrophotometer. All water was doubly distilled and deionised prior to use.

### **Irradiation sources**

Initial irradiations were carried out using one of two high powered light emitting diodes (LEDs) purchased from RS Components. The LEDs are characterised by emission peaks at either: **365 nm** (HBW = 10 nm; LED Engin, LZ1 UV LED 365 nm Gen 2 (maximum wattage = 2.8 W), **617 nm** (HBW = 14 nm; Thorlabs High-Power LED M617D2 (maximum wattage = 2.2 W). The emission spectra of the LEDs were recorded using a spectroradiometer (model: OL756, Gooch & Housego) and are illustrated in figure 1, below, along with the absorbance spectrum for MB (10<sup>-5</sup> mol L<sup>-1</sup>) in aqueous solution.



**Figure 1:** – Emission spectra of the 365 and 617 nm LEDs (HBW = 10 and 14 nm, respectively) and the bandgap energy for anatase TiO<sub>2</sub> (broken red line). Also shown (broken blue line) is the absorbance spectrum for MB in aqueous solution (10<sup>-5</sup> mol L<sup>-1</sup>). The intensity of each LED has been normalised to the peak LED emission output, measured with respect to power (i.e.  $\mu\text{W cm}^{-1} \text{ eV}^{-1}$ ).

The typical irradiance value exhibited by each LED was also determined using this spectroradiometer. In this work the LEDs were placed 2 cm away from the reaction dispersion under test, contained in a 1 cm cuvette, and yielded a beam size of ca. 5 cm, with irradiances of 5 and 15 mW cm<sup>-2</sup> for the 365 and 617 nm LEDs, respectively. The diffuse reflectance spectra of pressed discs of the neat semiconductor photocatalysts were recorded using a Konica Minolta CM-2500d spectrophotometer.

#### Initial solution irradiations using TiO<sub>2</sub>

Three different 100 cm<sup>3</sup> test solutions were prepared for the irradiation studies using 365 and 617 nm LEDs, namely: (1) **TiO<sub>2</sub> plus SED**: i.e. 0.05 mg cm<sup>-3</sup> TiO<sub>2</sub> + 10 wt.% glycerol, (2) **TiO<sub>2</sub> alone**: i.e. 0.05 mg cm<sup>-3</sup> TiO<sub>2</sub> and (3) **SED alone**: i.e. 10 wt.% glycerol. The resulting solution/suspensions were stirred using a magnetic flea for 30 min to ensure the glycerol was dissolved and the TiO<sub>2</sub> was uniformly dispersed.

For each irradiation, the sample under test, i.e. one of the solutions (1) – (3), was purged with argon under constant stirring for 10 minutes, after which 3 cm<sup>3</sup> of the solution were

transferred to an argon purged, 1 cm cuvette equipped with a crown-shaped stirrer (VWR, product no: 442-0502). To this sample, a 30  $\mu\text{L}$  plug of an Ar purged aqueous solution of MB ( $1 \times 10^{-3} \text{ M}$ ) was injected to give an initial dye concentration of  $1 \times 10^{-5} \text{ mol L}^{-1}$ . The cuvette was then sealed with a plastic lid and parafilm wrapped, to prevent air leaking into the reaction cell, and placed inside a UV-vis spectrophotometer under constant stirring, using a magnetic stirrer, where it was irradiated *in-situ* with either a 365 or 617 nm radiation from an appropriate LED, positioned inside the spectrophotometer, perpendicular to the monitoring light path to the detector and 2 cm away from the cuvette. The photo-induced change in absorbance of the dye-containing sample solution under test was monitored spectrophotometrically as a function of irradiation time,  $t$ . After irradiation of the sample, the cuvette was exposed to the air under constant stirring, and any oxygen-sensitive recovery of the original colour of the MB was monitored spectrophotometrically also as a function of time.

### Action spectra irradiations

The action spectra reported in this work were recorded using a Xe KiloArc lamp (OBB Corp.), fitted with a monochromator as the light source. Thus, this system was used to provide selected irradiation bands of radiation, with peaks at  $\lambda(\text{exc})$  (units: nm), and Half Peak Band Width = 10 nm. This system was used to irradiate the photocatalyst system under test at different wavelengths, spanning the range 350 - 740 nm. In this work the irradiation area,  $\sigma$ , was  $1 \text{ cm}^2$ . The photoreactor comprised a 1 cm quartz cell, containing  $3.0 \text{ cm}^3$  of the reaction solution which were stirred continuously as described above. The reaction solution was analysed using a UV/Vis spectrophotometer so as to yield data for the subsequent plot of absorbance (at 665 nm) vs irradiation time decay profiles for each excitation wavelength. These plots were used to provide values for the initial rates of MB bleaching (i.e.  $r$ , units: molecules MB bleached  $\text{s}^{-1}$ ) at the different  $\lambda(\text{exc})$ . In all of this work, the reaction solution comprised: an aqueous dispersion ( $0.05 \text{ mg cm}^{-3}$ ) of P25  $\text{TiO}_2$ , or CdS, in which there was also  $10^{-5} \text{ mol L}^{-1}$  MB.

As before, all light emission spectra were recorded using a high-performance, **calibrated** UV-Vis OL 756 spectroradiometer (Gooch & Housego), equipped with an integrating sphere. The area under the recorded emission spectrum, for each selected excitation wavelength band,  $\lambda(\text{exc})$ , generated by the Xe lamp/monochromator system, and used to irradiate the

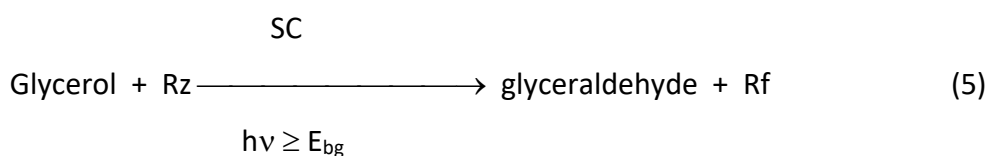
reaction solution, was used to determine the total irradiance value,  $I(\lambda)$ ; units:  $\text{mW cm}^{-2}$ , for each  $\lambda(\text{exc})$  band. In the action spectrum studies, the value of the photonic efficiency at each  $\lambda(\text{exc})$ , i.e.  $\eta$ , was calculated using the following expression:

$$\eta = r / \{ \lambda(\text{exc}) \times 1.84 \times 10^{15} \times I(\lambda) \times \sigma / 365 \} \quad (4)$$

where  $\sigma = 1 \text{ cm}^2$ .

### The photocatalysed reduction of methylene blue.

In recent years, this group has developed a rapid, simple method for assessing the activities of UVA-absorbing photocatalytic **films**, involving the use of photocatalyst activity indicator inks (*paiis*) [13-15]. The most used and effective of these *paiis* employs the blue-coloured, redox dye, Resazurin (Rz), which is readily, and irreversibly, reduced by photogenerated electrons on the  $\text{TiO}_2$ , to the pink-coloured dye, resorufin (Rf) [13,14]. Rz, like MB, absorbs little in the UVA region, but does have a significant peak (molar absorptivity = ca.  $47000 \text{ M}^{-1} \text{ cm}^{-1}$  [16]) at ca. 602 nm. This reduction reaction is accompanied by the rapid and irreversible reduction of the photogenerated holes by glycerol (i.e. glycerol is a SED), which is also present in the ink film. As a consequence, the overall photocatalytic process is as follows:

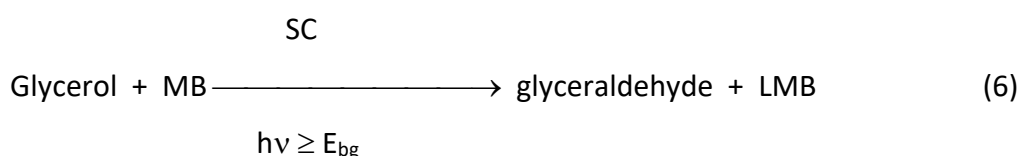


where, in the case above, SC is usually  $\text{TiO}_2$  and  $h\nu$  = UV radiation, most typically of wavelength 365 nm, i.e. UVA radiation. Other work has established the existence of a direct correlation in the rate of photocatalysed reduction of Rz in an Rz *paii*, *via* reaction (3) with that of the photocatalysed oxidation of a thin solid organic film (stearic acid) or MB in solution, *via* reaction (1), when mediated by a  $\text{TiO}_2$  film, and electronically excited using UVA radiation [14,17]. Typically, the Rz *paii* test is completed within a few minutes, and so is much faster than any of the more traditional tests based on reaction (1). For example, the Rz *paii* test is typically 45 times faster than the MB in solution ISO test [3], when using commercial,  $\text{TiO}_2$ -coated, self-cleaning glass.



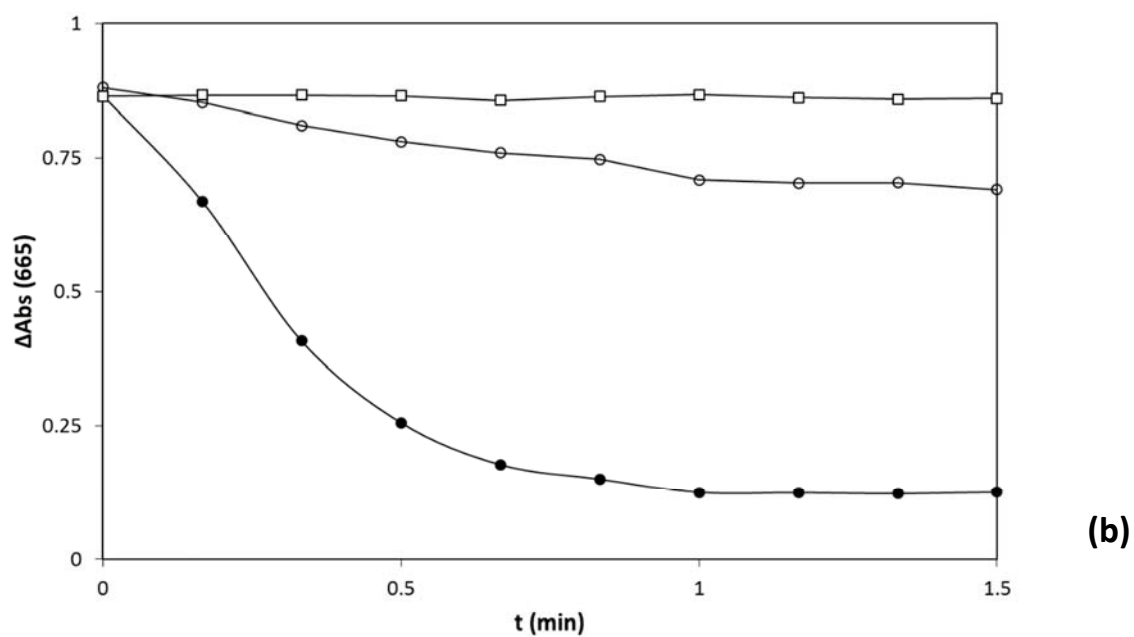
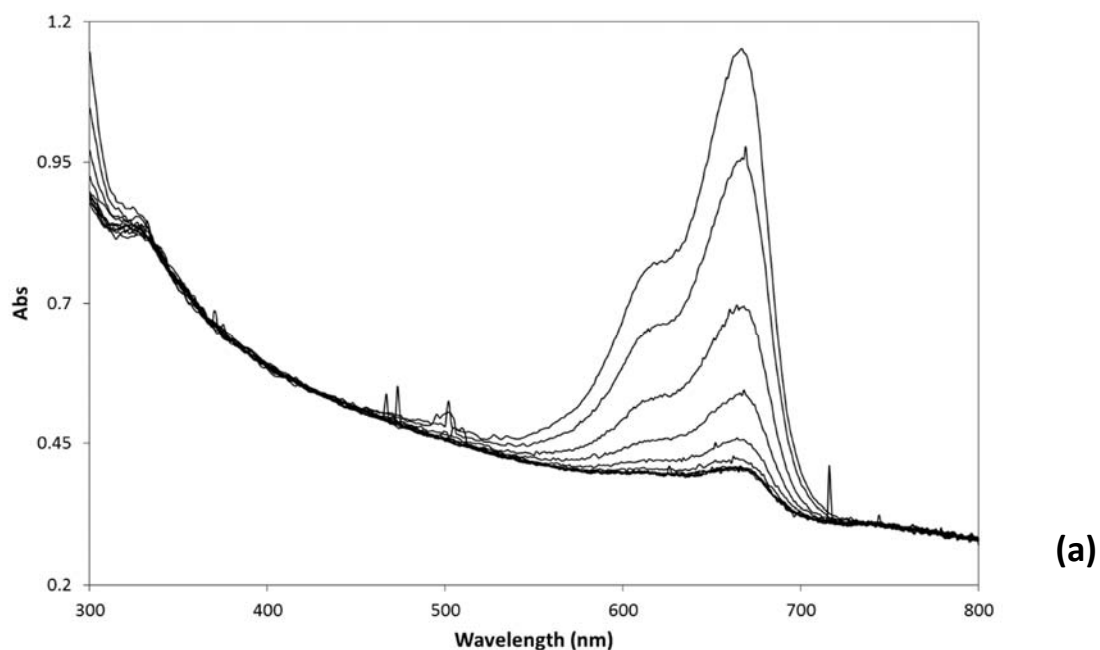
The reaction that underpins the Rz ink test, i.e. reaction (5), is an example of *reductive* photocatalysis [13] in that the primary species under observation, Rz, is reduced. In contrast, reaction (1), in general, and the MB ISO reaction in particular, are examples of *oxidative* photocatalysis, since the primary species, e.g. MB, is oxidized [13]. Note, however, that in both cases, i.e. reactions (1) and (5), the overall process is a photocatalysed *redox* reaction.

If MB is used instead of Rz in reaction (5), then the colourless species, *leuco* emthylene blue (LMB) is likely to be produced, i.e.



And since LMB is easily re-oxidised to MB by O<sub>2</sub>, then obviously reaction (6) needs to be conducted under anaerobic conditions [18]. Interestingly, the absence of O<sub>2</sub> also ensures that the traditional dye-sensitised bleaching reaction, reaction (2), cannot occur, which, in turn suggests that it should be possible to probe the activity of a photocatalytic material using a dye, like MB, *via* a *photoreductive* process carried out under anaerobic solution, since the observed dye bleaching can only be due to the photocatalytic reaction (6), assuming dye photolysis is negligible [19].

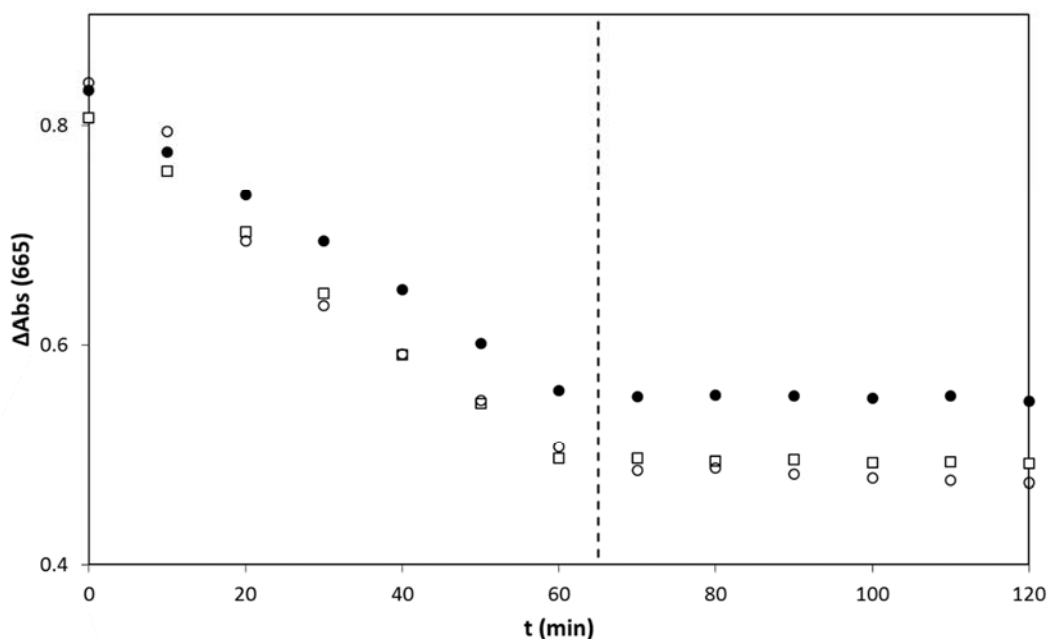
In order to test this proposal, a series of simple initial reactions were conducted in which an anaerobic dispersion of P25 TiO<sub>2</sub> (0.05 mg cm<sup>-3</sup>), in the presence of 10<sup>-5</sup> mol L<sup>-1</sup> MB was irradiated using UVA radiation (365 nm LED; 5 mW cm<sup>-2</sup>), in either the absence, or presence, of the sacrificial electron donor, glycerol (10 wt %). Figure 2(a) illustrates the typical change in UV/Vis absorption spectrum of the TiO<sub>2</sub>/MB/glycerol solution from which it is clear that the MB is rapidly photobleached *via* reaction (6), i.e. within 1.5 min. Proof that LMB was the major product of this photocatalysed bleaching process was obtained by subsequently exposing the photobleached dispersion, in the dark, to air. This action led to the rapid re-oxidation of the LMB to MB, allowing the MB to regain 92% of its original blue colour, as measured by its absorbance at 665 nm. The recorded change in the initial absorbance of the TiO<sub>2</sub>/MB/glycerol solution at 665 nm, ΔAbs(665), as a function of irradiation time is illustrated in figure 2(b), closed circles.



**Figure 2:** 365 nm, 5 mW cm<sup>2</sup> irradiation: (a) UV/Vis spectra of the TiO<sub>2</sub> (0.05 mg cm<sup>-3</sup>)/MB (10<sup>-5</sup> mol L<sup>-1</sup>)/glycerol (10 wt%) system recorded every 10 s during irradiation (top to bottom); (b) ΔAbs(665) vs. irradiation time plots for Ar-purged 10<sup>-5</sup> mol L<sup>-1</sup> MB aqueous solutions that contain: (□) 10 wt% glycerol, but no photocatalyst, (○) TiO<sub>2</sub> (0.05 mg cm<sup>-3</sup>), but no glycerol, and (●) TiO<sub>2</sub> (0.05 mg cm<sup>-3</sup>) + glycerol (10 wt%).

An identical irradiation of the same anaerobic system, but without  $\text{TiO}_2$ , i.e. MB/glycerol, produced no loss in colour, as illustrated by the recorded  $\Delta\text{Abs}(665)$  vs.  $t$  plot in figure 2(b), suggesting that the electronically excited state of MB is not quenched by glycerol. In contrast, when the  $\text{TiO}_2$ /MB system, i.e. no SED, is irradiated for 1.5 min, a small amount of photobleaching does occur, as illustrated by the  $\Delta\text{Abs}(665)$  vs.  $t$  plot in figure 2(b). This result appears surprising, since there is no obvious SED present, nor any  $\text{O}_2$  present. However, this effect has been noted before by this group and is attributed to the MB itself acting as the SED in reaction (6), in the absence of glycerol [20]. Some evidence for this is provided by the observation that when the partially photobleached  $\text{TiO}_2$ /MB system was aerated in the dark, only 64% of the colour loss was regained, compared to 92% when glycerol was present, thereby suggesting that the remaining 36% had been permanently photobleached, presumably by acting as the SED in reaction (6), instead of glycerol.

If the anaerobic MB/glycerol system is to have any promise as a dye-based test system for UV AND Visible-absorbing photocatalytic materials, then it needs to be shown that it doesn't exhibit evidence of a non-photocatalytic dye bleaching process, due to electronic excitation of the dye, over the timescale of a typical irradiation. In order to demonstrate this feature, the same systems as described above (see figure 2), namely:  $\text{TiO}_2$ /MB/glycerol,  $\text{TiO}_2$ /MB and MB/glycerol, were irradiated with visible light which the MB dye, but not the semiconductor, will absorb significantly, namely 617 nm; 15 mW  $\text{cm}^{-2}$  light provided by an LED. The subsequent plots of the  $\Delta\text{Abs}(665)$  vs.  $t$  generated in this study are illustrated in figure 3 and reveal that the dye undergoes a very slow bleaching process (ca. 42% decay over 60 min) at a rate that is largely independent of the presence, or absence, of either glycerol or  $\text{TiO}_2$ , suggesting that it is due to dye photolysis, i.e. reaction (3), and not dye sensitisation. Further evidence that this is the case is provided by the observation that aeration, in the dark, of each of these partially photobleached systems produces no recovery in colour of the MB, suggesting that no LMB is produced during the course of the photobleaching reactions illustrated in figure 3, and that the bleaching of the MB under these conditions is permanent, as expected for reaction (3).



$\Delta\text{Abs}(665)$  vs. irradiation time plots for Ar-purged  $10^{-5}$  mol L<sup>-1</sup> MB aqueous solutions that contain: (□) 10 wt% glycerol, but no photocatalyst, (○)  $\text{TiO}_2$  ( $0.05 \text{ mg cm}^{-3}$ ), but no glycerol, and (●)  $\text{TiO}_2$  ( $0.05 \text{ mg cm}^{-3}$ ) + glycerol (10 wt%). The broken line highlights when the light was switched off.

More importantly is the observation that this photolytic dye-bleaching process, using 617 nm light, is much slower (ca. 240 times) than that of reaction (6), mediated by P25  $\text{TiO}_2$  using 365 nm light, even though the irradiance at 617 nm is ca. 3 times more than that used at 365 nm. These findings suggest that the MB/glycerol system has potential as a dye-based test system for UV AND Visible-absorbing photocatalytic materials provided the photocatalyst under test is sufficiently active that the rate of dye bleaching in the absence of photocatalyst is negligible over the time period of the test.

### Action spectra

A greater appreciation of this potentially new, dye-based test system can be gleaned from a study of the action spectrum of the MB/glycerol test system using a UV-absorbing and a Visible-absorbing photocatalyst, namely: P25  $\text{TiO}_2$  and CdS, respectively. In this work, the photonic efficiency,  $\eta$ , of the semiconductor for mediating reaction (6) was determined as a function of excitation wavelength,  $\lambda$ , where  $\eta$  is defined as [21]:

$$\eta = r_i/\rho \quad (7)$$

where,  $r_i$  = initial rate, (units: moles of MB photobleached  $\text{s}^{-1}$ ) and  $\rho$  = incident photon flux, (units: moles of photons of wavelength,  $\lambda$ , or Einsteins  $\text{s}^{-1}$ ); in this work, the average irradiance was  $3.2 \text{ mW cm}^{-2}$ . At each excitation wavelength, the initial rate of MB photobleaching,  $r_i$ , was calculated from the measured decay in the absorbance of the MB at 665 nm over the first 30 s of irradiation. The parameter,  $\rho$ , was measured using a calibrated spectroradiometer at each excitation wavelength. The action spectra arising from this work, for the  $\text{TiO}_2/\text{MB}/\text{glycerol}$  and  $\text{CdS}/\text{MB}/\text{glycerol}$  systems, are illustrated in figures 4(a) and 4(b), respectively. Both spectra show no evidence of dye bleaching at 665 nm, i.e. at the  $\lambda_{\text{max}}$  of MB, indicating that dye-excited state processes, such as dye-sensitisation and dye photolysis, are not significant over the irradiation timescale (i.e.  $2 \text{ min} \leq t$ ) used in this study.

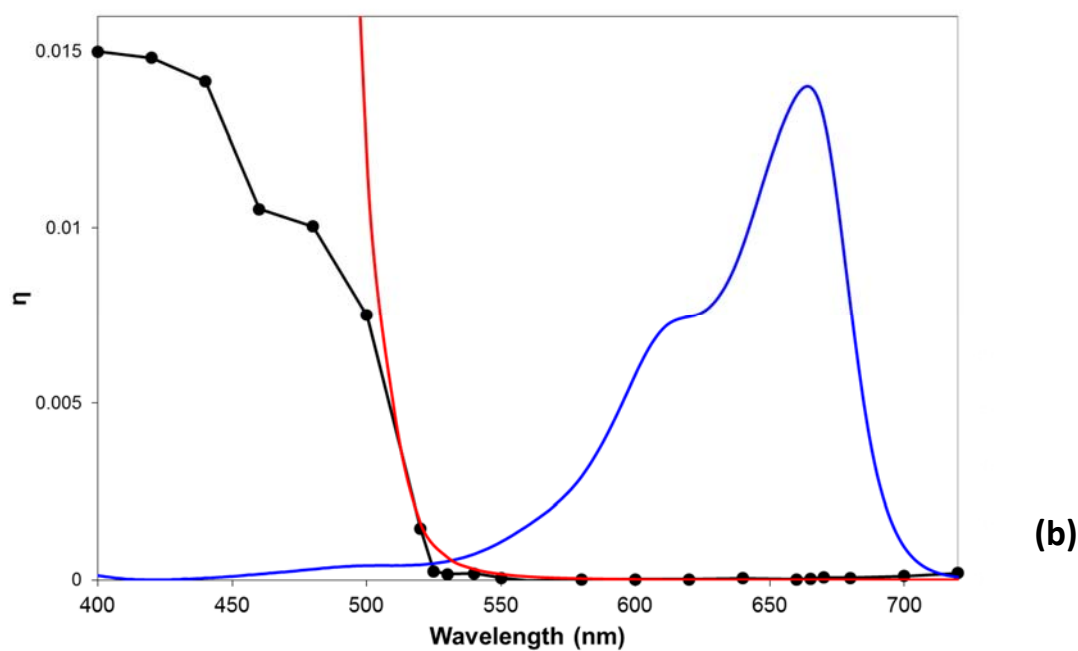
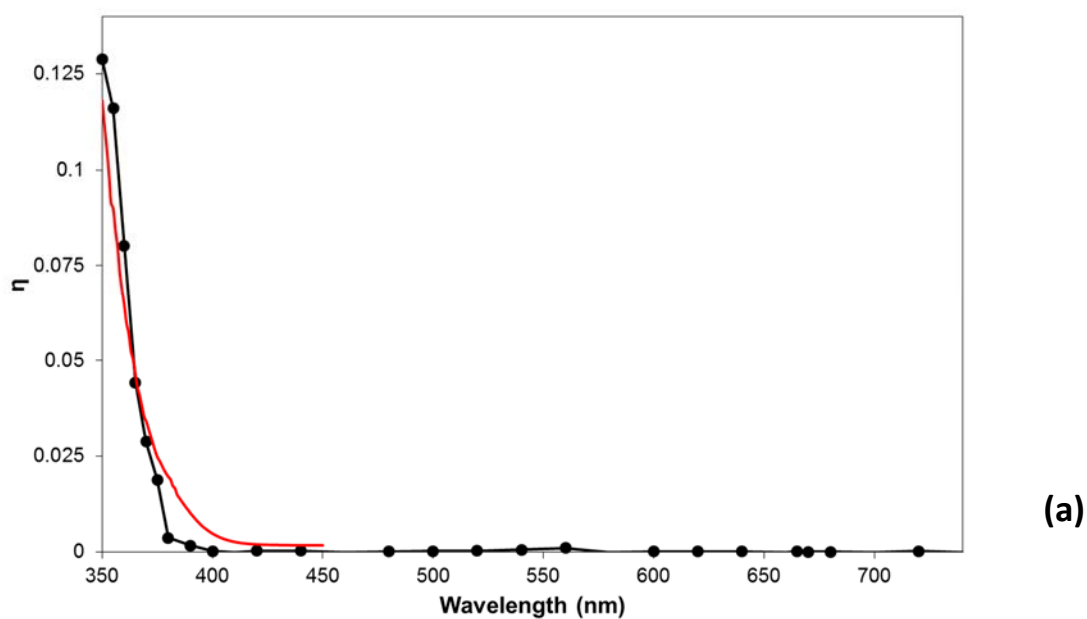
It can be shown that for an ideal photocatalytic system, in which  $r_i$  is proportional to  $\rho$  at all  $\lambda$  absorbed by the semiconductor, that:

$$\eta = kf \quad (8)$$

where  $k$  is a proportionality constant, which depends upon [MB] and the intrinsic activity of the photocatalyst, i.e. the probability that an absorbed photon leads to reaction, and where  $f$  is the fraction of light absorbed by the semiconductor photocatalyst. If it is assumed that  $k$  is independent of excitation wavelength, as suggested by classical semiconductor band theory [22], in which the photogenerated charge carriers are thermalized before reacting, then the action spectrum of an ideal photocatalytic system should have the same shape as the plot of  $f$  vs  $\lambda$ , which, in turn, should be similar to a Kubelka-Munk plot of the diffuse reflectance spectrum, or absorption, spectrum of the semiconductor.

Other work carried out on the  $\text{TiO}_2/\text{MB}/\text{glycerol}$  (using 365 nm radiation) and  $\text{CdS}/\text{MB}/\text{glycerol}$  (using 400 nm radiation) systems, in which the initial rate was measured as a function of irradiance, over the range  $0.5\text{-}3 \text{ mW cm}^{-2}$ , revealed, in both cases, that  $r_i$  is proportional to irradiance, and so the calculated photonic activities of both systems, as illustrated in figure 4, should be described by eqn (8), at all wavelengths absorbed by the semiconductors. Evidence that this is indeed the case is provided by the good match of the broken red lines and solid black lines illustrated in figures 4(a) and 4(b), which correspond to

the Kubelka-Munk plot of the diffuse reflectance spectra, DRS, and action spectra, of the  $\text{TiO}_2$  and CdS dispersions, respectively. The good correlation between the DRS and the action spectra for both  $\text{TiO}_2$  and CdS, provides strong evidence that in both cases the semiconductor photocatalyst is the light absorbing species responsible for driving the dye photobleaching reaction forward. In all cases, after photobleaching, the subsequent exposure of the reaction solutions to air promoted the almost (> 95%) complete recovery of the original solution's colour and absorbance spectrum due to MB, thereby indicating that LMB was the major product and that, for both  $\text{TiO}_2$  and CdS, the photobleaching reaction is due to reaction (6).



**Figure 4:** Action spectra (black line) of (a)  $\text{TiO}_2/\text{MB}/\text{glycerol}$  and (b)  $\text{CdS}/\text{MB}/\text{glycerol}$  systems, the red broken lines are the diffuse reflectance spectra of the (a)  $\text{TiO}_2$  and (b)  $\text{CdS}$  dispersions. The red and blue lines correspond to the DRS (Kubelka-Munk plot) of the semiconductor and Visible absorption spectra of the  $10^{-5} \text{ mol L}^{-1}$  MB solution, respectively.

## Conclusions

The anaerobic photocatalysed reduction of MB by glycerol to LMB shows no evidence of dye-sensitisation, nor rapid dye photolysis, when used with either a UV-only or visible-absorbing photocatalyst, such as P25 TiO<sub>2</sub> and CdS, respectively. Instead, the action spectra reveal a spectral sensitivity that matches very well with that of the DRS's of the respective semiconductor photocatalysts. The photocatalysed reaction is facile and leads to a striking colour change, blue to colourless, that can be readily reversed in the dark by simply allowing air into the system, so as to effect the oxidation of the photogenerated LMB back to its original blue, oxidized form, MB. The overall *reductive* photocatalytic reaction that is responsible for the photo-induced changes in colour described above is summarized by reaction (6). Like the photocatalyst activity indicator ink technology for photocatalyst *films*, the MB/glycerol system appears to offer a simple, quick and unambiguous way to assess the photocatalytic activity of both visible and UV absorbing photocatalyst *powders*, even using a dye such as MB, which is notorious for exhibiting photobleaching due to sensitization, when used in an aerobic solution, in the absence of a SED.

Of course, a key feature of the semiconductor photocatalyst in reaction (1) is the ability to reduce oxygen. Thus, it can be argued that for this dye-based method of assessment to be useful in probing SCs for reaction (1), rather than providing a measure of photocatalytic activity per se, it is necessary to show for different SCs that the kinetics of the photocatalytic reaction (1) correlate with those for reaction (6). Since the redox potential for the reduction of MB at pH 7, i.e. MB/LMB (0.011V) [23] at pH 7. whereas that for oxygen depends how many electrons are transferred, e.g. 4e<sup>-</sup>: O<sub>2</sub>/H<sub>2</sub>O (0.815 V, 2e<sup>-</sup>: O<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> (0.281 V) and 1e<sup>-</sup>: O<sub>2</sub>/O<sub>2</sub><sup>-</sup> (-0.33) [24], it is not obvious that a SC capable of reducing MB to LMB will be able to reduce O<sub>2</sub>. It follows that further work is necessary to see how useful this dye-reduction test is in probing the ability of a semiconductor to photocatalyse reaction (1). Promisingly, recent work carried out using the Rz ink on pressed powers of a variety of different semiconductors, such as TiO<sub>2</sub>, CdS, WO<sub>3</sub> and C<sub>3</sub>N<sub>4</sub>, suggests that such a correlation does exist for reaction (5) at least, which is not so dissimilar to reaction (6) [19].



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